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Acidity and activity of H-ZSM-5 measured with NH_3 -t.p.d. and n-hexane cracking

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NH_3 -t.p.d. and n-hexane cracking were used to characterize the acidity and activity of zeolite H-ZSM-5. From the NH_3 -t.p.d. experiments it could be concluded that two types of acid sites are present in H-ZSM-5: Weak acid sites corresponding with desorption at low temperature and small ΔH_{des} , and strong acid sites corresponding with desorption at high temperature and large ΔH_{des} . Especially the desorption at high temperature could be explained satisfactorily by theoretical models as presented in literature. From the n-hexane cracking experiments information about the initial activity and the deactivation were obtained. Combination of the results of both methods led to a relation between the initial activity and the amount of strong acid sites. However, it was impossible to relate the deactivation with one of the acidic properties.

Keywords: H-ZSM-5; acidic properties; NH_3 -t.p.d; n-hexane cracking

INTRODUCTION

The acidity of zeolites can be investigated by several methods. With infrared spectroscopy one can determine whether Lewis or Brønsted sites are present¹. From results obtained it may be concluded that the ZSM-5 samples used in this work contain mainly Brønsted acid sites.

The acid strength can be determined by measuring the heat of adsorption or desorption of a suitable probe molecule. Ammonia meets the requirements for such a probe. Firstly it is small enough to enter all the zeolite pores. Secondly it can react both with the Brønsted and Lewis acid sites. Pyridine, for instance is much less suitable with regard to the first requirement.

The heat of adsorption can be measured with calorimetry and the heat of desorption with temperature programmed desorption (t.p.d.). During adsorption, NH_3 enters the zeolite and adsorbs at the first available site. This is not necessarily the strongest one. In this way too low a value of the acid strength is obtained. During desorption starting with all sites covered, ammonia will first desorb from the weakest site. Therefore t.p.d., in theory the most correct method, is applied in this work.

Although t.p.d. is a well known method, not so much has been reported about it using zeolites, especially ZSM-5. A satisfying theory for determining the heat of desorption from the t.p.d. plot is developed by Cvetaňovic and Amenomiya³. Gorte⁴ and Alnot¹⁹ reported that the

method of a sequence of measurements with different heating rates gives the most reliable values for the heat of desorption. Using this method Topsøe¹ has already reported NH_3 t.p.d. for ZSM-5.

The cracking of n-hexane is used as a test reaction to determine the activity and the deactivation of the catalyst. As has been shown earlier⁶ this simple reaction can be used for testing the suitability of ZSM-5 for methanol conversion. In this work an attempt is made to find the relation between the acidity, measured with NH_3 -t.p.d. and the catalytic behaviour of ZSM-5. Variation of the acidity is achieved by variation of the Al content⁵ and by changing the degree of exchange.

EXPERIMENTAL

Synthesis

ZSM-5 catalysts were synthesized in a Teflon vessel placed in an autoclave, under autogeneous pressure (5–6 atm) for 6 days at 150°C. A typical reaction mixture was $\text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{Na}_2\text{O} : \text{K}_2\text{O} : \text{TPAOH} : \text{H}_2\text{O} = 1 : 59 : 1.25 : 0.87 : 12.5 : 1200$. Where Al_2O_3 and Na_2O are supplied as sodium aluminate, SiO_2 as colloidal silica, and TPAOH as a 20% aqueous solution also containing K_2O . With respect to the original recipe⁷, lowering of the TPAOH content enhanced the crystallinity (from XRD). Silicalite, the Al-free ZSM-5⁹, was also synthesized. After crystallization the ZSM-5 was calcined (air, 550°C for 3 h) to remove the organic material. Crystallinity, checked with XRD⁷ was

Table 1

Samples	Chemical composition			n-hexane cracking		NH ₃ -t.p.d.			
	SiO ₂ /Al ₂ O ₃	N _{Al,uc} *	excht†	k ₀ (h ⁻¹)	λ (10 ⁻²)	HTP		LTP	
						ΔH _{des} (kJ mol ⁻¹)	N (10 ²⁰ sites/g)	ΔH _{des}	N
E1	22.1	8.0	0.75	0.56	2.80				
E3	22.1	8.0	0.85	0.92	1.63	73	1.8	45	5.7
F1	49.5	3.7	0.52	0.48	4.98	116	1.3	103	3.4
F2	49.5	3.7	0.81	0.67	4.29				
F3	49.5	3.7	0.89	0.65	4.21	169	1.8	109	3.3
H1	68.8	2.7	0.88	0.51	4.17				
H3	68.8	2.7	0.97	0.46	3.03	138	0.9	76	2.0
I1	41.0	4.5	0.96	1.20	19.6				
I3	41.0	4.5	0.98	1.43	25.8	137	2.8	68	6.1

* N_{Al,uc} = number of Al per unit cell (Al_xSi_{96-x}O₁₉₂)

† exch = (mol Al - mol (Na + K))/mol Al

good for all samples. To exchange the Na⁺ and K⁺ ions for H⁺ the ZSM was stirred for 1 h with a 2 M NH₄OH solution at 80°C, washed and calcined. To obtain different degrees of exchange this was done 1–3 times. The catalysts used in this work are summarized in Table 1.

Apparatus and procedure

n-Hexane cracking

The n-hexane cracking was carried out in a tubular quartz reactor. The n-hexane was fed in the He carrier-gas stream by a syringe pump and led over the catalyst at 300°C. The flow of n-hexane was 1 g/((g catalyst) h). The reactor bed contained 0.5 g ZSM-5, particle size 60–125 μm. The reaction product was chromatographically analysed, every 25 min for at least 4 h.

NH₃-t.p.d.

The apparatus used for NH₃-t.p.d. is schematized in Figure 1. Before adsorption the catalyst (0.5 g)

was dried in a flow of 23 ml min⁻¹ of predried He for 2 h. Adsorption took place with 20% NH₃ in the He flow at 70°C for 0.5 h. Finally the catalyst was flushed with He at 70°C for 1 h. Desorption was done by heating the catalyst from 70°C to 600°C with a linear heating schedule. The amount of desorbing NH₃ was measured with a heat conductivity detector. The exit gas was bubbled through a gas-washing-bottle filled with 0.1 N H₂SO₄ to collect the NH₃, so the total amount could be determined by back titration.

RESULTS AND DISCUSSION

n-Hexane cracking

The cracking of the n-hexane as function of the time on stream is shown in Figure 2. Because the cracking is first order in n-hexane¹⁵ it follows that:

$$\frac{dC}{dt} = -kC \quad (1)$$

$$k = -\frac{1}{\tau} \ln \frac{C_{out}}{C_{in}} = -\frac{1}{\tau} \ln (1 - x) \quad (2)$$

In these equations the rate constant k is time dependent to discount the deactivation. Several theoretical models are in use to describe the course of k as a function of the reaction time. These models have in common that k can be characterized by two parameters: the initial rate constant k_0 , and the deactivation constant λ . Although it is possible to describe mathematically each curve, the model which is of interest uses only these two parameters. Unfortunately the models we used^{12,13} gave a poor fit for the conversion curves and so far as we know there are no models which describe properly conversion with zeolite catalysts in terms of both initial activity and deactivation. In spite of this there is still a need to compare the catalysts so the k_0 values are determined by graphical extrapolation and λ by

Figure 1 NH₃-t.p.d. apparatus

Figure 2 n-Hexane cracking versus time on stream

the following equation:

$$\lambda = \frac{k_0 - k_{(t=3\text{ h})}}{3} \quad (3)$$

The results are given in Table 1. They show that except for the samples H₁ and H₃ activity increases with increasing degree of exchange. Such a relationship cannot be found for deactivation. XRD and adsorption of n-butane were used to examine the crystallinity of the zeolites. As mentioned before all samples show a good XRD crystallinity and there was no significant difference between them. The pore volume determination with n-butane adsorption (at 23°C) resulted for all samples in values between 0.162 and 0.173 ml g⁻¹, which is in good agreement with other investigations^{10,11}. So it is also not possible to explain the differences in catalytic behaviour by differences in crystallinity.

As expected, silicalite shows no activity in the n-hexane test. Only 1–2% isomerization occurred. The acidity of silicalite comes from the ≡Si—OH groups at the external crystal surface and is far too weak for n-hexane cracking.

NH₃-t.p.d.

Figure 3 shows a typical t.p.d. plot. The catharometer response in arbitrary units which is proportional to the desorption rate r , is given as a function of the desorption temperature.

With the theory developed by Cvetanovic and Amenomiya³ it is possible to determine the activation energy E_{des} or the heat ΔH_{des} of desorption. The investigations of Gorte⁴ for the design parameters of t.p.d. apparatus show that this theory is applicable in our experimental set-up and that

freely occurring readsorption is most likely. The desorption rate is given by:

$$r = -\frac{d\theta}{dt} = \nu\theta^n \exp\left(\frac{-E_{\text{des}}}{RT}\right) \quad (4)$$

The coverage θ equals unity when all available adsorption sites are covered. The desorption is first order if $\log r/\theta$ versus $1/T$ gives a linear relationship. Figure 4 shows that this holds very well for the high temperature peak (HTP) but not for the low temperature peak (LTP). T.p.d. plots

Figure 3 NH₃-t.p.d. plot for catalyst I3 detector response versus temperature

Figure 4 $\log S/\theta$ versus $1000/T$ belonging to the t.p.d. plot of Figure 3. S is the catharometer response in arbitrary units

of silicalite only possess the LTP, so combined with the fact that silicalite does not crack n-hexane makes it clear that only the HTP is of catalytic interest. Because NH_3 desorption is first order, in the HTP, and readsorption occurs freely, the relation between the peak maximum temperature T_m and the heat of desorption ΔH_{des} is given by³:

$$2 \log T_m - \log \beta = \frac{\Delta H_{\text{des}}}{2.303 RT_m} + \log \left| \frac{(1 - \theta_m) V_s \Delta H_{\text{des}}}{\text{FAR}} \right| \quad (5)$$

where β is the linear heating rate.

An analogous relation between T_m , β and E_{des} is only valid in the case where readsorption does not occur, which is not very likely in microporous catalysts⁴. Because E_{ad} from gases to a solid surface is negligible ΔH_{des} is almost equal to E_{des} . If the t.p.d. curves are recorded with various heating rates β , ΔH_{des} can be determined according to relation (5) by plotting $2 \log T_m - \log \beta$ against $1/T_m$. This was done for the LTP and the HTP.

Determination of T_m and the peak area is done by computer fitting the measured t.p.d. plot with the theoretical curve shape³, which will be discussed later. Results are summarized in Table 1.

The values of ΔH_{des} obtained with NH_3 -t.p.d. using different heating rates are in good agreement with microcalorimetric measurements of Auroux⁵ comparing ΔH_{des} for the HTP found in this work with their initial heat of adsorption. There is good agreement with Topsøe¹ however they used the equation for activation energy¹. Applying one heating rate and estimating the last term of relation (5) or using relation (4) gives deviating and unreliable results.

ΔH_{des} as a function of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio appears to have a maximum at $\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 50$ (which agrees with Ref. 11). From structural considerations one would understand an increase of acidity with increasing ratio until a top level is reached at a ratio of 48 because then there is one Al at each pore intersection, in case of random distribution. But, however, it shows that acidity is a function of Al content. The number of both strong and weak acid sites (N_{htp} and N_{ltp}) increases with the Al content. The strong increase of the weak acid sites makes it clear that these sites cannot only be silanol ($\equiv \text{Si}-\text{OH}$) surface sites.

Plotting the initial rate-constant k_0 of n-hexane cracking versus the N_{htp} (Figure 7) gives an almost linear relationship. Also for the LTP there is a clear increase of k_0 with N_{ltp} . The k_0 has no

Figure 5 $2 \log T_m - \log \beta$ versus $1000/T_m$ for catalyst 13. $\beta = 15.21, 12.63, 9.51, 6.43$ and 1.22 from left to right for the indicated points

Figure 6 Amount of desorbed molecules NH_3 versus the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for the LTP and the HTP of the catalyst (Table 1)

Figure 7 Initial rate constant k_0 versus sites/g catalyst for the LTP and HTP of the catalyst (Table 1)

relation with ΔH_{des} . So it seems that for n-hexane cracking it is mainly the number of strong acid sites which is important and not the strength.

The deactivation constant λ of the catalyst cannot be related with any other parameter. Only with some caution can it be stated that λ increases with the number of acid sites. To discover if coke formation at the external surface is the cause of deactivation^{6,14}, and is a function of the crystallite surface acidity, t.p.d. was done with another probe molecule. Triethylamine (TEA) was used instead of NH_3 . This is too large to enter the ZSM-5 pores but has the same basic properties as NH_3 . For TEA-t.p.d. the same procedure was followed as for NH_3 -t.p.d. Again there is a HTP ($T_m \approx 490^\circ\text{C}$) and a LTP ($T_m \approx 180^\circ\text{C}$) and silicalite only possesses the LTP. However, the relation between TEA-t.p.d. (external surface acidity) and deactivation is not better than for NH_3 -t.p.d.

CURVE FITTING

The Cvetanovic and Amenomiya model

It is possible that the NH_3 -t.p.d. plot consists of more than the two peaks which are visible at first sight. Depending on the heating rate, some catalysts showed a weak shoulder after the top of the LTP. Therefore attempts are made to resolve the curve with the model for the case of desorption with freely occurring readsorption. With their theory they derived an equation for the concentration C of the desorbing species in flowing gas as a function of surface coverage. To obtain C , which is proportional to the catharometer response, as a function of the temperature (at linear heating rate) the following equations have to be evaluated:

$$-\frac{\ln(\theta_m/\theta_i) - (\theta_m - \theta_i)}{(1 - \theta_m)^2} = \epsilon_m \exp(\epsilon_m) \times \int_0^1 \exp\left(-\frac{\epsilon_m}{T_n}\right) dT_n \quad (6)$$

$$\epsilon_m = \frac{\Delta H_{\text{des}}}{RT_m} \quad X = \epsilon_m \left(1 - \frac{1}{T_m}\right)$$

$$\ln(\theta) - \theta = \ln(\theta_m) - \theta_m$$

$$-(1 - \theta_m)^2 \int_0^x \frac{e^x}{(1 - x/\epsilon_m)^2} dx \quad (7)$$

$$C_n = \frac{\theta}{1 - \theta} \frac{1 - \theta_m}{\theta_m} e^x \quad (8)$$

Starting with an initial coverage $\theta_i = 1$, C as a

function of T can be computed. By varying ϵ_m the theoretical curve can be fitted to the ascending slope of the first experimental peak. With the fitting ϵ_m the theoretical descending slope is computed. After subtracting the theoretical curve from the experimental one, the procedure is repeated for the remaining curve. The result is shown in Figure 3a. It is possible to connect to each peak a ΔH_{des} value by applying different heating-rates as described before. This results in decreasing ΔH_{des} values for peaks with increasing T_m , which is physically impossible. Furthermore not every catalyst shows the same number of resolved peaks. So this way of curve resolving is not very reliable. If the theory is valid, it should also be possible to resolve the curve in the opposite direction from high to low temperature (Figure 8b). In this way a direct resolving of the HTP, which is of catalytic interest, is obtained. With this method the HTP area is determined, for the LTP area the total area minus the HTP area is taken. The poor fit of the LTP makes it clear that the theoretical model cannot be applied for the whole plot.

Figure 8 (a) T.p.d. curve resolving for catalyst 13, in forward direction (b) T.p.d. curve resolving for catalyst 13, in backward direction

Because the theoretical curve shape is assymmetric with respect to T_m , curve resolving gives a better method of determining the HTP peak area.

CONCLUSIONS

The cracking of n-hexane has been used to determine the activity and deactivation of ZSM-5. This reaction seems to have a threshold level for acid strength. Above this level the acidity only depends on the number of acid sites. Therefore translation of n-hexane activity and deactivation to other chemical reactions has to be done with great care. To examine the relation between deactivation and acidity a better model for deactivation then applied in this work is needed.

NH₃-t.p.d. is a useful method for characterizing the acidity of a catalyst in terms of acid strength (ΔH_{des}) and the number of acid sites. For reliable values of ΔH_{des} the method of different heating rates has to be applied. It was not possible to relate the strong or weak acid sites to discrete lattice positions. With curve resolving according to Cvetanovic and Amenomiya it is not possible to distinguish in a proper manner more than two acid strengths. Applying backwards curve resolving rather than just determining the peak maximum temperature is a more accurate way of determining the area of the HTP.

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NOMENCLATURE

k	rate constant (g n-hexane/g catalyst h)
k_0	rate constant $t = 0$
t	contact time (h)
WHSV	weight hourly space velocity (g n-hexane/g catalyst h)
C	concentration in = reactor in out = reactor out
X	conversion
λ	deactivation constant (h^{-1})
E_{des}	activation energy for desorption (kJ/mol K)
H_{des}	heat of desorption (kJ mol ⁻¹)
r_{des}	rate of desorption
ν	frequency factor
θ	coverage
n	order
T_m	peak maximum temperature (K)
β	heating rate (K min ⁻¹)
N_{htp}	number of NH ₃ desorbing in the high temperature peak
N_{ltp}	number of NH ₃ desorbing in the low temperature peak
index	i initial m at peak maximum n normalized to peak maximum (e.g. $T_n = T/T_m$)

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